

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-154521

(43)Date of publication of application : 09.06.1998

(51)Int.Cl.

H01M 8/02

H01M 4/86

H01M 8/10

(21)Application number : 09-243802

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(22)Date of filing : 09.09.1997

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(30)Priority

Priority number : 08251084

Priority date : 24.09.1996

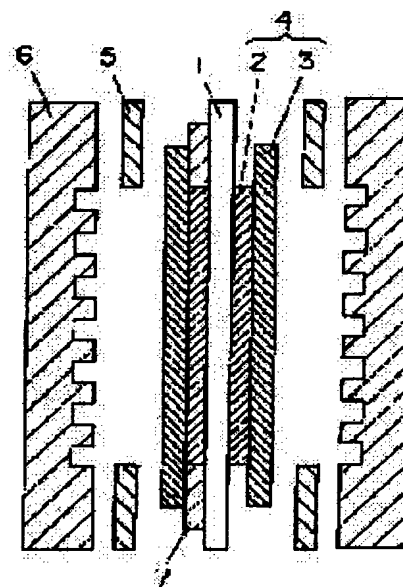
Priority country : JP

(54) SOLID HIGH POLYMER TYPE FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent damage of an ion exchange membrane, and improve sealing performance of a fuel cell by setting a thickness of the ion exchange membrane to a specific thickness, making the area of a catalyst layer smaller than a diffusive layer in a gas diffusive electrode, making a peripheral part of the catalyst layer exist on the inside of the diffusive layer, and providing an architrave-shaped protective film at least on one surface side in the ion exchange membrane.

SOLUTION: The area of a catalyst layer 2 is made smaller than the area of a diffusive layer 3. A fuel cell comprises an ion exchange membrane 1 having a gas diffusive electrode 4 where a peripheral edge part of the catalyst layer 2 exists on the inside of a peripheral edge part of the diffusive layer 3 and an architrave-shaped reinforcing film 7 where a window frame coincident with a shape of the catalyst layer 2 is arranged, at least one both sides of one. By such a constitution, an edge part of the electrode diffusive layer 3 can be made to coincide with a part where the reinforcing film 7 exists without reducing the contact area of the reinforcing film 7 and the ion exchange membrane 1 whose thickness is not more than 50 micron.



LEGAL STATUS

[Date of request for examination]

15.03.2004

[Date of sending the examiner's decision of
rejection]

[Kind of final disposal of application other than
the examiner's decision of rejection or
application converted registration]

[Date of final disposal for application]

[Patent number] 3805495

[Date of registration] 19.05.2006

[Number of appeal against examiner's decision
of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] It is the polymer electrolyte fuel cell which has the open beam frame-like reinforcement film for the aperture whose ion exchange membrane the periphery section of a catalyst bed is inside the periphery section of a diffusion layer, and thickness of ion exchange membrane is 50 micrometers or less in the polymer electrolyte fuel cell equipped with the gas diffusion electrode which consists of the catalyst bed prepared in both sides of ion exchange membrane and said ion exchange membrane, and a diffusion layer, and corresponds with the configuration of a catalyst bed in one [at least] field side.

[Claim 2] The polymer electrolyte fuel cell according to claim 1 which supplies a positive electrode by oxidant gas and supplies fuel gas to a negative electrode by no humidifying.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates especially to the ion exchange membrane of a polymer electrolyte fuel cell about a polymer electrolyte fuel cell.

[0002]

[Description of the Prior Art] The polymer electrolyte fuel cell (it is henceforth described as PEFC) uses the precious metal catalyst for the electrolyte for the ion exchange membrane which is a solid-state polyelectrolyte as an electrode catalyst.

[0003] When hydrogen is used as a fuel in PEFC, the reaction of (** 1) occurs in a negative electrode.

[0004]

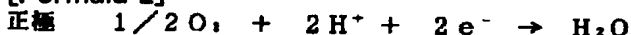
[Formula 1]



[0005] Moreover, when oxygen is used as an oxidizer, in a positive electrode, the reaction of (** 2) occurs and water is generated.

[0006]

[Formula 2]



[0007] If ion exchange membrane is not a certain water content more than fixed, and (** 1) (** 2) will not show ion conductivity, and a reaction will not occur. Moreover, if water content is low even if ion conductivity is shown, resistance of ion exchange membrane will become large and an output will decrease by IR loss. Therefore, in PEFC, in order to fully carry out the water of the ion exchange membrane, fuel gas and oxidant gas are humidified and supplied. In order that the water used for humidification may prevent contamination of the film or a catalyst, impurities, such as the organic substance, and a chloride ion, a metal ion, must not be contained, but conductivity must be the pure water of 10 to 2 or less Scms. Since humidification water is consumed with actuation of PEFC, makeup is needed. In order to exclude makeup of this pure water, there is a system (United States patent No.5,200,278) which is made to circulate through reactant gas and collects water, but in order to prevent mixing of an impurity, a system, such as preparing the filter of ion exchange resin, becomes complicated.

[0008] To application to the small noncommercial use power source of PEFC, in order to consider as a simpler system, humidify[no]-izing of reactant gas is desirable. However, ion exchange membrane is not fully humidified only by no humidifying-izing [reactant gas], but resistance becomes large, and a property falls. In order to solve this problem, the ion exchange membrane is made to humidify with the water which was made to carry out the direct reaction of the hydrogen and oxygen which are made to contain noble metals and a metal oxidation particle, and cross in an ion exchange membrane, and generated them in the ion exchange membrane (JP,7-90111,A). At this time, 30-200 micrometers of thickness of ion exchange membrane are preferably set to 50-100 micrometers.

[0009] However, if the thickness of ion exchange membrane becomes thin at about 50 micrometers, the crossover to which reactant gas passes through ion exchange membrane will start, and an electrical potential difference will fall. Drawing 3 is the sectional view of the conventional polymer electrolyte fuel cell. The electrode 4 which becomes both sides of ion exchange membrane 1 from a catalyst bed 2 and the diffusion tub 3 is arranged, a gasket 5 is arranged at the periphery section of an electrode 4, a separator 6 **** these, and the cell is constituted. There is nothing that supports ion exchange membrane 1 between an electrode 4 and a gasket 5. Therefore, when the thickness of ion exchange membrane was thin, the following nonconformities arose. Mechanical stress might start ion exchange membrane on the occasion of the assembly of a cell, and ion exchange membrane might be damaged. Moreover, at the time of actuation, expansion and contraction of the ion exchange membrane of the perimeter part of an electrode start by change and desiccation of the water content of a film-electrode zygote. Stress might be started and damaged to ion exchange membrane by this dimensional change. Furthermore, ion exchange membrane might be torn by the pressure differential of fuel gas and oxidant gas. Moreover, when joining an ion exchange membrane to an electrode with a hotpress, the ion exchange membrane might be damaged with the edge of the diffusion layer of an electrode. If ion exchange membrane is damaged as mentioned above, oxidant gas will be mixed with fuel gas and the serious problem for safety, such as burning on a catalyst, will arise.

[0010] Then, the following amelioration has been made in order to prevent membranous breakage. The periphery section of an electrode and the rim section of the ion exchange membrane by which an electrode is not arranged are covered. And arrange the reinforcement film of gas impermeability so that it may lap with a gas-seal part (JP,5-242897,A). Make it unify with a sealant using the sealant of the shape of liquefied or a sheet so that it may lap with the perimeter of a front face of the electrode of a film-electrode zygote (JP,8-45517,A). Join a plate-like reinforcement member to a film-electrode zygote using a sealant (JP,7-65847,A). one field side of ion exchange membrane is equipped with the protective coat of the sheet of the shape of a frame which is stuck by the periphery section of ion exchange membrane, and has a lap in an electrode at least (JP,5-21077,A —) Use the ion exchange membrane which put 5 No. — 174845 official report and ion exchange membrane with small ion exchange capacity (it is described as henceforth E.W.) by the large ion exchange membrane of E.W., and was unified (JP,6-251780,A). It is the approach (JP,7-220742,A) of forming an auxiliary gasket in the periphery section of a diffusion layer by the sealant.

[0011]

[Problem(s) to be Solved by the Invention] However, when the thin ion exchange membrane of thickness was used, in order to reinforce with the configuration of above-mentioned JP,5-242897,A, JP,8-45517,A, and JP,7-65847,A at a film-electrode zygote, with it, it had the fault that breakage of the film with the edge of the diffusion layer at the time of joining the film to an electrode could not be prevented. Furthermore, with the configuration of JP,5-242897,A and JP,8-45517,A, since a protective coat or the seal section lapped with an electrode, it had the fault that the area to which reactant gas is supplied became smaller than an electrode surface product. Moreover, with the configuration of JP,5-21077,A and JP,5-174845,A which are shown in drawing 4 , since an electrode 4 is joined to the ion exchange membrane 1 which has the reinforcement film 7, breakage of the ion exchange membrane 1 at the time of junction can be prevented. However, since the reinforcement film 7 existed between the electrode catalyst bed 2 and ion exchange membrane 1, it had the fault that the effective area of an electrode 4 and ion exchange membrane 1 decreased. Moreover, there is futility of joining expensive ion exchange membrane to a part without the ion conductivity need with the configuration of JP,6-251780,A, and the spreading process of a sealant is complicated with the configuration of JP,7-220742,A.

[0012] Moreover, with the above-mentioned conventional configuration for non-humidified operation, hydrogen was consumed by the chemical reaction and it had the fault that the utilization factor of hydrogen fell.

[0013] This invention solves such a conventional technical problem, also when a thin film is used, breakage of ion exchange membrane is prevented, and it aims at offering the polymer electrolyte fuel cell which raised seal nature. The polymer electrolyte fuel cell which operates by no

humidifying is offered without furthermore reducing a hydrogen utilization factor.

[0014]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, as for the polymer electrolyte fuel cell of this invention, the thickness of ion exchange membrane uses a thing 50 micrometers or less, in a gas diffusion electrode, the area of a catalyst bed shall be smaller than the area of a diffusion layer, and there shall be the periphery section of a catalyst bed inside the periphery section of a diffusion layer, and ion exchange membrane shall have an open beam frame-like protective coat for the aperture which is in agreement with the configuration of a catalyst bed in one [at least] field side.

[0015] Even when thickness uses the ion exchange membrane of 50 micrometers or less and a thin film by the above-mentioned configuration, breakage of ion exchange membrane can be prevented, without decreasing the effective area of an electrode and ion exchange membrane, and breakage of the film at the time of the assembly of a cell and actuation can be prevented, and seal nature can be raised.

[0016] Furthermore, the polymer electrolyte fuel cell of this invention is supplied to a positive electrode by oxidant gas, and supplies fuel gas to a negative electrode by no humidifying, respectively.

[0017] Since the absolute magnitude of the water for the concentration gradient of the water of a membrane electrode zygote becoming large by the above-mentioned configuration, humidifying [of ion exchange membrane] becoming easy since the diffusion (back-diffusion of gas) by the side of the negative electrode of the water generated with the positive electrode becomes easy to take place, and humidifying ion exchange membrane decreases, ion exchange membrane can fully be humidified only with generation water. For this reason, non-humidified actuation is attained, without making ion exchange membrane contain a noble-metals particle and a metallic-oxide particle.

[0018]

[Embodiment of the Invention] In the polymer electrolyte fuel cell equipped with the gas diffusion electrode which consists of the catalyst bed which formed the polymer electrolyte fuel cell of this invention in both sides of ion exchange membrane and said ion exchange membrane, and a diffusion layer, the periphery section of a catalyst bed is inside the periphery section of a diffusion layer, and thickness is 50 micrometers or less and ion exchange membrane is a polymer electrolyte fuel cell which has the open beam frame-like reinforcement film for the aperture which is in agreement with the configuration of a catalyst bed in one [at least] field side.

[0019] Cross-section structural drawing of the polymer electrolyte fuel cell of one example of this invention is shown in drawing 1 . As shown in drawing 1 , the area of a catalyst bed 2 is smaller than the area of a diffusion layer 3, and it consists of ion exchange membrane 1 which has the reinforcement film 7 of the shape of a frame which prepared the gas diffusion electrode 4 which has the periphery section of a catalyst bed 2 inside the periphery section of a diffusion layer 3, and the sash which is in agreement with the configuration of a catalyst bed 2 in one [at least] field side. 5 is a gasket and 7 is a separator.

[0020] By considering as such a configuration, since the reinforcement film 7 and the electrode catalyst bed 2 do not lap, the touch area of an electrode 4 and an ion exchange membrane 1 cannot be decreased, and the edge part of the electrode diffusion layer 3 can be located in the part in which the reinforcement film 7 exists. Therefore, even when thickness uses thin ion exchange membrane 50 micrometers or less, at the time of junction of the film and an electrode, breakage of the film at the time of the assembly of a cell and actuation is prevented, and it becomes possible to raise seal nature.

[0021] Furthermore, this invention is a polymer electrolyte fuel cell with which a positive electrode is supplied by oxidant gas and it supplies fuel gas to a negative electrode by no humidifying.

[0022] In a polymer electrolyte fuel cell, internal resistance becomes low and the outstanding cell property is shown, so that the ion exchange membrane of thin thickness is used.

Furthermore, by considering as such a configuration, the absolute magnitude of the water for humidifying ion exchange membrane becomes little, and the concentration gradient of water

becomes large, the back-diffusion of gas of generation water becomes easy, and ion exchange membrane can fully be humidified only with generation water. Therefore, the non-humidified actuation of this solid-state polyelectrolyte mold fuel cell is attained.

[0023] In addition, although one example of this invention of drawing 1 showed what has the the same configuration of a catalyst bed and the the same sash of a protective coat, what was mostly in agreement with the configuration of a catalyst bed shall be sufficient as a sash, and it shall not lap with a catalyst bed. Moreover, even if a clearance exists in the sash of a catalyst bed and a protective coat before assembly, it is possible for it to be also in agreement by binding each part article tight at the time of the assembly of a cell.

[0024] Moreover, although one example of this invention of drawing 1 showed what has the reinforcement film in one field side of ion exchange membrane, effectiveness with the same said of what has the reinforcement film in the both sides of ion exchange membrane as shown in drawing 2 is acquired.

[0025]

[Example] Hereafter, the example of this invention is explained, referring to a drawing.

[0026] (Example 1) The colloid dispersion liquid of the solid-state polyelectrolyte which mixed the alcoholic solution and organic solvent of a solid-state polyelectrolyte, and was agitated, and the carbon powder catalyst which made the platinum catalyst support were mixed, and it was made the shape of a paste, and applied on the carbon paper which gave a water-repellent finish with the fluororesin, and the forward negative electrode of the gas diffusion electrode which consists of a catalyst bed (50mmx50mm) and a diffusion layer (55mmx55mm) was created. The amount of platinum catalysts was made into 0.5 mg/cm² also with the forward negative electrode. Moreover, the amount of polyelectrolytes was made into 1.0 mg/cm² also with the forward negative electrode, and created the ion exchange membrane (80mmx80mm) equipped with the sash which is 50mmx50mm the catalyst bed and whose configuration corresponded with the reinforcement film (80mmx80mm). The hotpress of said electrode and ion exchange membrane was carried out by 120-150 degrees C and 20 - 200 kgf/cm², and the membrane electrode zygote was produced. The ion exchange membrane used Nafion112 (50 micrometers of thickness) by U.S. Du Pont. The reinforcement film was used as the sheet with adhesion material of a fluororesin with a thickness of 50 micrometers which prepared the sash of the same configuration as a catalyst bed, and was stuck on one side of ion exchange membrane. The cell A of the polymer electrolyte fuel cell equipped with the reinforcement film shown in drawing 1 using this zygote was produced.

[0027] (Example 1 of a comparison) The gas diffusion electrode which consists of 50mmx50mm the catalyst bed and diffusion layer of the same magnitude was created, except having used the ion exchange membrane (80mmx80mm) which is not equipped with the reinforcement film, it presupposed that it is the same as an example 1, and the cell B without the reinforcement film shown in drawing 3 was produced.

[0028] (Example 2 of a comparison) The cell C made the same as an example 1 was produced except having used Nafion115 (130 micrometers of thickness) by U.S. Du Pont for the ion exchange membrane.

[0029] (Example 3 of a comparison) Except having prepared the sash of the reinforcement film in 45mmx45mm so that the inner circumference of the reinforcement film might lap with the periphery section of a catalyst bed about 5mm, it presupposed that it is the same as an example 1, and the cell D shown in drawing 4 was produced.

[0030] (Example 2) It changed to Nafion112 (50 micrometers of thickness) by U.S. Du Pont which is the ion exchange membrane used in the example 1, and the cells E and F made the same as an example 1 were produced except having used Japan Gore-Tex GORE-SELECT (20 micrometers of thickness, 10 micrometers).

[0031] (Example 4 of a comparison) It changed to Nafion112 (50 micrometers of thickness) by U.S. Du Pont which is the ion exchange membrane used in the example 1 of a comparison, and the cells G and H made the same as the example 1 of a comparison were produced except having used Japan Gore-Tex GORE-SELECT (20 micrometers of thickness, 10 micrometers).

[0032] Above, hydrogen gas was supplied to the negative-electrode side of cell A-H of the

example of this invention, and the example of a comparison, air was supplied to the positive-electrode side, and the spark test in non-humidified actuation and humidification actuation was performed. In non-humidified actuation, both hydrogen gas and air were supplied without no humidifying and warming, and did not perform warming of a cell, either. Moreover, in humidification actuation, hydrogen gas humidified and supplied air to 40 degrees C at 60 degrees C, and operating temperature was made into 50 degrees C.

[0033] The number of breakage of the ion exchange membrane in the cells A, E, and F of the example of this invention and the cells B, D, and H of the example of a comparison is shown in a table 1.

[0034]

[A table 1]

	実 施 例			比 較 例			
単電池	A	E	F	B	D	G	H
破損数/全数	0/10	0/10	0/10	2/10	0/10	6/10	10/10

[0035] Air and hydrogen were supplied, and when generation of heat was looked at by the no-load cell, it was judged that ion exchange membrane was damaged. Although breakage of ion exchange membrane was looked at by 2 in 10 cells in the cell B which does not use the reinforcement film when 50-micrometer ion exchange membrane was used, breakage of ion exchange membrane was not looked at by the cells A and D using the reinforcement film. Moreover, in the case where 20-micrometer ion exchange membrane is used, although breakage of ion exchange membrane was looked at by 6 in 10 cells in the cell G which does not use the reinforcement film, breakage of ion exchange membrane was not looked at by the cell E using the reinforcement film. Although breakage of ion exchange membrane was looked at by all ten cells in the cell H which does not use the reinforcement film in the case where 10 more-micrometer ion exchange membrane is used, breakage of ion exchange membrane was not looked at by the cell F using the reinforcement film. When the reinforcement film was used, even if the thickness of ion exchange membrane was 50 micrometers or less, breakage did not arise from these results.

[0036] The current-voltage curve at the time of non-humidified actuation of the cells A, E, and F of the example of this invention and the cell C of the example of a comparison and humidification actuation is shown in drawing 5. Moreover, as compared with the time of humidification actuation, the cell voltage of non-humidified actuation fell with all cells. However, in dozens of mV and the cell C whose thickness is 130 micrometers to small one, the electrical-potential-difference difference was large and the sag in Cells A, E, and F fell remarkably with current density lower than especially 0.2 A/cm².

[0037] The current value at the time of non-humidified actuation of the cells A, E, and F of the example of this invention and the cell C of the example of a comparison and humidification actuation and the relation of internal resistance are shown in drawing 6. Moreover, although the internal resistance of non-humidified actuation increased with all cells as compared with the time of humidification actuation, as compared with Cells A, E, and F, the internal resistance of the large cell C of thickness increased remarkably.

[0038] In non-humidified actuation, ion exchange membrane is humidified only with generation water. There may be few moisture contents required in order to humidify ion exchange membrane so that thickness is small, if it is the same moisture content, as for the water content of ion exchange membrane, the direction of the film with thin thickness will become high, and

resistance will become small. Moreover, if thickness is small, the concentration gradient of water will become large, it becomes easy to carry out back-diffusion of gas of the water generated with the positive electrode, and ion exchange membrane becomes is easy to be humidified. The thickness of the ion exchange membrane used for the cell A of this example is as thin as 50 micrometers. Therefore, it can be said that Cell A showed the polarization property which internal resistance becomes [the water content of ion exchange membrane] comparatively high low also by non-humidified actuation, and does not have humidification actuation and inferiority. With the cells E and F using ion exchange membrane with still thinner thickness, such effectiveness becomes large, non-humidified actuation becomes easy, and it is thought that the property still higher than Cell A was shown. since Cell C, on the other hand, has the thickness of ion exchange membrane as thick as 130 micrometers — generation water — humidification of ion exchange membrane — inadequate — internal resistance — high — becoming — especially — generation — it appears notably in a low current consistency region with little amount of water, and the property of non-humidified actuation is considered to have fallen as compared with humidification actuation.

[0039] The current-voltage curve in non-humidified actuation of the cell A of the example of this invention and the cells B and D of the example of a comparison is shown in drawing 7 . The open-circuit voltage of Cells A, B, and D is 1015mV, 900mV, and 1010mV, respectively, and Cells A and D showed the value higher than Cell B. Moreover, Cells A and B are the almost same polarization properties, and showed the property superior to Cell D.

[0040] Since Cells A and D showed open-circuit voltage higher than Cell B, it can be said that the crossover of the reactant gas from the periphery of an electrode was controlled with the reinforcement film. Moreover, in Cell D, since the reinforcement film has lapped with the electrode catalyst bed, the area of an electrode and ion exchange membrane decreases. However, Cell A can be said to have shown the polarization property which ion exchange membrane was reinforced and was superior to Cell D, without an electrode surface product decreasing, since the reinforcement film does not lap with an electrode catalyst bed.

[0041] In addition, although the Nafion film by U.S. Du Pont and Japan Gore-Tex GORE-SELECT were used for the ion exchange membrane in this example, if it is the ion exchange membrane which shows cation conductivity, it will not be limited to this.

[0042] Moreover, although the fluororesin sheet was used for the reinforcement film, the same effectiveness will be acquired if it has thermal resistance and acid resistance. Although the sheet which has adhesion material was used in this example, the same effectiveness is acquired also by uniting with ion exchange membrane the sheet which does not have adhesion material by thermal melting arrival etc. Although the reinforcement film with a thickness of 50 micrometers was furthermore used by this example, it is necessary to restrict the thickness of the reinforcement film with the thickness in an example, but to optimize it with the thickness of ion exchange membrane.

[0043] Although the periphery section of the reinforcement film and the periphery section of ion exchange membrane are furthermore in agreement by this example, the same effectiveness will be acquired if the periphery section of the reinforcement film is outside the periphery section of a gaseous diffusion layer.

[0044]

[Effect of the Invention] As mentioned above, without decreasing the reaction area of an electrode, when the ion exchange membrane of a thin film is used, according to this invention, at the time of membrane electrode junction, breakage of ion exchange membrane can be prevented at the time of cell assembly and actuation, and the polymer electrolyte fuel cell which has the outstanding seal nature can be realized.

[0045] Moreover, it becomes possible to perform non-humidified actuation of a polymer electrolyte fuel cell, without the hydrogen utilization factor by making hydrogen and oxygen react in ion exchange membrane decreasing.

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平10-154521

(43) 公開日 平成10年(1998) 6月9日

(51) Int. Cl. ⁶

識別記号

F I

H01M 8/02

H01M 8/02

E

S

4/86

4/86

M

8/10

8/10

審査請求 未請求 請求項の数 2 O L (全7頁)

(21) 出願番号 特願平9-243802

(22) 出願日 平成9年(1997) 9月9日

(31) 優先権主張番号 特願平8-251084

(32) 優先日 平8(1996) 9月24日

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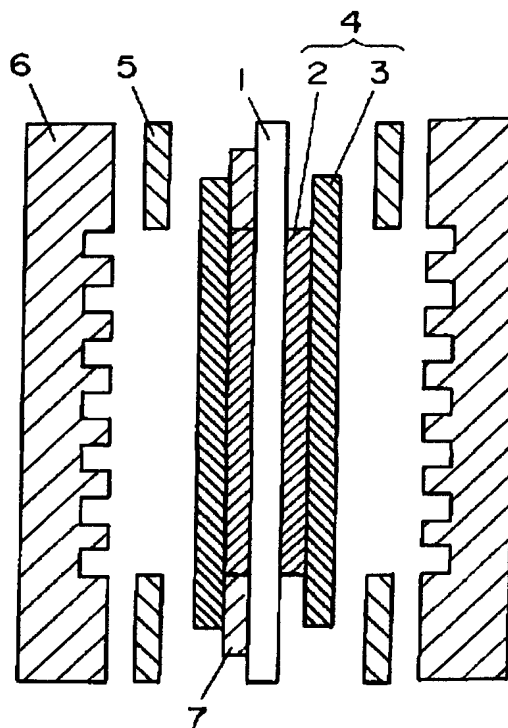
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(54) 【発明の名称】 固体高分子型燃料電池

(57) 【要約】

【課題】 膜厚の薄いイオン交換膜を用いてもイオン交換膜の破損が無く、また水素利用率を低下させず無加湿で作動する固体高分子型燃料電池を実現する。

【解決手段】 イオン交換膜の膜厚を50 μ m以下で、触媒層の面積を拡散層より小さくした電極と、触媒層と同一の形状の窓枠を設けた補強膜を少なくとも片面に有するイオン交換膜とを用いることにより、無加湿で作動しかつイオン交換膜の破損のない固体高分子型燃料電池が得られる。



【特許請求の範囲】

【請求項1】 イオン交換膜と前記イオン交換膜の両面に設けた触媒層と拡散層から成るガス拡散電極を備えた固体高分子型燃料電池において、触媒層の周縁部は拡散層の周縁部の内側にあり、かつイオン交換膜は厚みが50 μ m以下であり、イオン交換膜は触媒層の形状と一致する窓を開けた額縁状の補強膜を少なくとも一方の面側に有する固体高分子型燃料電池。

【請求項2】 正極に酸化剤ガス、負極に燃料ガスを無加湿で供給する請求項1記載の固体高分子型燃料電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、固体高分子型燃料電池に関するものであり、特に固体高分子型燃料電池のイオン交換膜に関するものである。

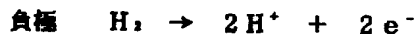
【0002】

【従来の技術】固体高分子型燃料電池（以降、PEFCと記す）は電解質に固体高分子電解質であるイオン交換膜を、電極触媒として貴金属触媒を用いている。

【0003】PEFCでは水素を燃料とした場合、負極では（化1）の反応が起こる。

【0004】

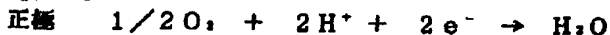
【化1】



【0005】また、酸素を酸化剤とした場合、正極では（化2）の反応が起こり、水が生成される。

【0006】

【化2】



【0007】イオン交換膜はある一定以上の含水率でなければイオン伝導性を示さず、（化1）および（化2）の反応が起こらない。またイオン導電性を示しても含水率が低ければイオン交換膜の抵抗は大きくなり、IR損により出力が減少する。そのためPEFCではイオン交換膜を十分に含水させるために燃料ガスと酸化剤ガスとを加湿して供給する。加湿に用いられる水は膜や触媒の汚染を防ぐために、有機物や塩素イオン、金属イオンなど不純物を含有せず、伝導度が 10^{-2} S/cm以下の純水でなければならない。加湿水はPEFCの作動と共に消費されるので補給が必要となる。この純水の補給を省くために、反応ガスを循環させて水を回収するシステム

（米国特許No. 5,200,278）があるが、不純物の混入を防ぐためにイオン交換樹脂のフィルターを設けるなどシステムが複雑になる。

【0008】PEFCの小型民生用電源への応用には、より単純なシステムとするために反応ガスの無加湿化が望ましい。しかし単に反応ガスを無加湿化するだけではイオン交換膜が十分に加湿されず抵抗が大きくなり、特性が低下する。この問題を解決するためにイオン交換膜中に貴金属と金属酸化微粒子を含有させてクロスオーバ

ーする水素と酸素をイオン交換膜中で直接反応させて生成した水でイオン交換膜を加湿させている（特開平7-90111号公報）。このときイオン交換膜の厚みは30~200 μ m、好ましくは50~100 μ mとしている。

【0009】しかしながら、イオン交換膜の膜厚が50 μ m程度に薄くなると反応ガスがイオン交換膜を通り抜けるクロスオーバーがおり、電圧が低下する。図3は従来の固体高分子型燃料電池の断面図である。イオン交換膜1の両面に触媒層2と拡散層3からなる電極4が配置され、電極4の外周部にガスケット5が配置され、これらをセパレータ6が挟持し単電池を構成している。電極4とガスケット5との間にはイオン交換膜1を支持するものがない。そのためイオン交換膜の膜厚が薄いと以下のような不具合が生じた。電池の組立の際にイオン交換膜に機械的ストレスがかかりイオン交換膜が破損することがあった。また作動時には膜-電極接合体の含水率の変化や乾燥によって電極の周囲部分のイオン交換膜の膨張・収縮が起こる。この寸法変化でイオン交換膜にストレスがかかり、破損することがあった。さらには燃料ガスと酸化剤ガスの圧力差によってイオン交換膜が破れることがあった。また電極とイオン交換膜をホットプレスで接合する際に電極の拡散層のエッジでイオン交換膜が損傷することがあった。前述したようにイオン交換膜が破損すると燃料ガスと酸化剤ガスが混合し触媒上で燃焼したりするなど安全性に重大な問題が生じる。

【0010】そこで、膜の破損を防ぐために以下のような改良がなされてきた。電極の周縁部と電極の配置されないイオン交換膜の外縁部とを被覆し、かつガスシール部分と重なるようにガス不透過性の補強膜を配置する

（特開平5-242897号公報）、膜-電極接合体の電極の表面周囲に重なるように液状あるいはシート状のシール材を用いてシール材と共に一体化させる（特開平8-45517号公報）、膜-電極接合体に平板状の補強部材をシーラントを用いて接合する（特開平7-65847号公報）、イオン交換膜の周縁部に密着されかつ電極に重なりをもつ額縁状のシートの保護膜を少なくともイオン交換膜の一方の面側に備える（特開平5-21077号公報、5-174845号公報）、イオン交換容量（以降E.W.と記す）の小さいイオン交換膜をE.W.の大きいイオン交換膜で挟み込んで一体化したイオン交換膜を用いる（特開平6-251780号公報）、拡散層の周縁部にシール材によって補助ガスケットを形成する（特開平7-220742号公報）などの方法である。

【0011】

【発明が解決しようとする課題】しかしながら、膜厚の薄いイオン交換膜を用いる場合、上記の特開平5-242897号公報、特開平8-45517号公報および特開平7-65847号公報の構成では膜-電極接合体に

補強を行うため、電極と膜を接合する際の拡散層のエッジによる膜の破損を防止できないという欠点を有していた。さらに特開平 5-242897 号公報および特開平 8-45517 号公報の構成では保護膜またはシール部が電極と重なるため、反応ガスが供給される面積が電極面積より小さくなるという欠点を有していた。また図 4 に示す特開平 5-21077 号公報および特開平 5-174845 号公報の構成では、補強膜 7 を有するイオン交換膜 1 に電極 4 を接合するので接合時のイオン交換膜 1 の破損は防止できる。しかしながら電極触媒層 2 とイオン交換膜 1 の間に補強膜 7 が存在するため電極 4 とイオン交換膜 1 の有効面積が減少するという欠点を有していた。また特開平 6-251780 号公報の構成ではイオン伝導性の必要のない部分に高価なイオン交換膜を接合するという無駄があり、特開平 7-220742 号公報の構成ではシール材の塗布工程が煩雑である。

【0012】また、無加湿運転のための上記従来の構成では水素が化学反応によって消費され、水素の利用率が低下するという欠点を有していた。

【0013】本発明はこのような従来の課題を解決するものであり、薄膜を用いた場合にもイオン交換膜の破損を防止し、シール性を向上させた固体高分子型燃料電池を提供することを目的とするものである。さらに水素利用率を低下させることなく無加湿で作動する固体高分子型燃料電池を提供するものである。

【0014】

【課題を解決するための手段】上記の課題を解決するために本発明の固体高分子型燃料電池は、イオン交換膜の厚みが $50\mu\text{m}$ 以下のものを用い、ガス拡散電極においては触媒層の面積が拡散層の面積より小さく、かつ触媒層の周縁部が拡散層の周縁部の内側にあり、イオン交換膜は触媒層の形状と一致する窓を開けた額縁状の保護膜を少なくとも一方の面側に有するものとする。

【0015】上記の構成によって膜厚が $50\mu\text{m}$ 以下と薄膜のイオン交換膜を用いた場合でも、電極とイオン交換膜との有効面積を減少させることなくイオン交換膜の破損を防ぐことができ、かつ電池の組立時および作動時の膜の破損を防ぎシール性を向上させることができる。

【0016】さらに本発明の固体高分子型燃料電池は、正極に酸化剤ガス、負極に燃料ガスをそれぞれ無加湿で供給するものである。

【0017】上記構成によって膜電極接合体の水の濃度勾配が大きくなり、正極で生成した水の負極側への拡散（逆拡散）が起こりやすくなるため、イオン交換膜の加湿が容易となり、かつイオン交換膜を加湿するための水の絶対量が減少するため、生成水のみで十分にイオン交換膜を加湿できる。このためイオン交換膜に貴金属微粒子と金属酸化物微粒子を含有させることなく無加湿作動が可能となる。

【0018】

【発明の実施の形態】本発明の固体高分子型燃料電池は、イオン交換膜と前記イオン交換膜の両面に設けた触媒層と拡散層から成るガス拡散電極を備えた固体高分子型燃料電池において、触媒層の周縁部は拡散層の周縁部の内側にあり、かつイオン交換膜は厚みが $50\mu\text{m}$ 以下であり、触媒層の形状と一致する窓を開けた額縁状の補強膜を少なくとも一方の面側に有する固体高分子型燃料電池である。

【0019】図 1 に本発明の一実施例の固体高分子型燃料電池の断面構造図を示す。図 1 に示すように触媒層 2 の面積が拡散層 3 の面積より小さく、かつ触媒層 2 の周縁部が拡散層 3 の周縁部の内側にあるガス拡散電極 4 と、触媒層 2 の形状と一致する窓枠を設けた額縁状の補強膜 7 を少なくとも一方の面側に有するイオン交換膜 1 とからなる。5 はガasket、7 はセパレータである。

【0020】このような構成とすることにより、補強膜 7 と電極触媒層 2 とが重ならないため電極 4 とイオン交換膜 1 との接触面積を減少させることがなく、かつ電極拡散層 3 のエッジ部分は補強膜 7 の存在する部分に位置させることができる。よって膜厚が $50\mu\text{m}$ 以下の薄いイオン交換膜を用いた場合でも、膜と電極の接合時、電池の組立時および作動時の膜の破損を防止し、シール性を向上させることが可能となる。

【0021】さらに本発明は、正極に酸化剤ガス、負極に燃料ガスを無加湿で供給する固体高分子型燃料電池である。

【0022】固体高分子型燃料電池において、薄い膜厚のイオン交換膜を用いるほど内部抵抗は低くなり、優れた電池特性を示す。さらに、このような構成とすることによって、イオン交換膜を加湿するための水の絶対量が少量となり、かつ水の濃度勾配が大きくなって生成水の逆拡散が容易となって生成水のみで十分にイオン交換膜を加湿できる。よってこの固体高分子型燃料電池は無加湿作動が可能となる。

【0023】なお図 1 の本発明の一実施例では、触媒層の形状と保護膜の窓枠が同じものを示したが、窓枠は触媒層の形状とほぼ一致したものでも良く、触媒層と重ならないものとする。また、組立前には触媒層と保護膜の窓枠に隙間が存在しても、電池の組立時に各部品を締め付けることにより一致することも可能である。

【0024】また図 1 の本発明の一実施例では、補強膜がイオン交換膜の一方の面側にあるものを示したが、図 2 に示すように補強膜がイオン交換膜の両側にあるものも同様の効果が得られる。

【0025】

【実施例】以下、本発明の実施例について、図面を参照しながら説明する。

【0026】（実施例 1）固体高分子型燃料電池のアルコー溶液と有機溶媒とを混合、攪拌した固体高分子型燃料電池のコロイド状分散液と白金触媒を担持させた炭素粉末触

媒とを混合してペースト状にし、フッ素樹脂で撥水处理を行ったカーボンペーパー上に塗布し、触媒層(50mm×50mm)と拡散層(55mm×55mm)から成るガス拡散電極の正負極を作成した。白金触媒量は正負極とも0.5mg/cm²とした。また高分子電解質量は正負極とも1.0mg/cm²とし、触媒層と形状が一致した50mm×50mmの窓枠を備えた補強膜(80mm×80mm)付きのイオン交換膜(80mm×80mm)を作成した。前記電極とイオン交換膜とを120~150℃、20~200kgf/cm²でホットプレスし、膜電極接合体を作製した。イオン交換膜は米国デュポン社製のNafion112(膜厚50μm)を用いた。補強膜は触媒層と同一の形状の窓枠を設けた厚み50μmのフッ素樹脂の粘着材付きシートとし、イオン交換膜の片面に貼り付けた。この接合体を用いて図1に示した補強膜を備えた固体高分子型燃料電池の単電池Aを作製した。

【0027】(比較例1) 50mm×50mmの同じ大きさの触媒層と拡散層から成るガス拡散電極を作成し、補強膜を備えないイオン交換膜(80mm×80mm)を用いた以外は実施例1と同じとし、図3に示した補強膜のない単電池Bを作製した。

【0028】(比較例2) イオン交換膜に米国デュポン社製のNafion115(膜厚130μm)を用いた以外は実施例1と同じとした単電池Cを作製した。

【0029】(比較例3) 補強膜の内周が触媒層の周縁部と約5mm重なるように補強膜の窓枠を45mm×4

5mmに設けた以外は実施例1と同じとし、図4に示した単電池Dを作製した。

【0030】(実施例2) 実施例1で用いたイオン交換膜である米国デュポン社製のNafion112(膜厚50μm)に換え、ジャパンゴアテックス(株)製のGORE-SELECT(膜厚20μm、および10μm)を用いた以外は実施例1と同じとした単電池EおよびFを作製した。

【0031】(比較例4) 比較例1で用いたイオン交換膜である米国デュポン社製のNafion112(膜厚50μm)に換え、ジャパンゴアテックス(株)製のGORE-SELECT(膜厚20μm、および10μm)を用いた以外は比較例1と同じとした単電池GおよびHを作製した。

【0032】以上本発明の実施例および比較例の単電池A~Hの負極側に水素ガスを、正極側に空気を供給して無加湿作動および加湿作動での放電試験を行った。無加湿作動では水素ガスおよび空気は共に無加湿、加温なしで供給し、単電池の加温も行わなかった。また加湿作動では水素ガスは60℃で空気は40℃に加湿して供給し、作動温度は50℃とした。

【0033】表1に本発明の実施例の単電池A、EおよびFと比較例の単電池B、DおよびHにおけるイオン交換膜の破損数を示す。

【0034】

【表1】

	実施例			比較例			
単電池	A	E	F	B	D	G	H
破損数/全数	0/10	0/10	0/10	2/10	0/10	6/10	10/10

【0035】空気および水素を供給し、無負荷の単電池に発熱が見られればイオン交換膜が破損していると判断した。50μmのイオン交換膜を用いた場合、補強膜を用いない単電池Bでは10セル中2セルにイオン交換膜の破損が見られたが、補強膜を用いた単電池AおよびDにはイオン交換膜の破損は見られなかった。また20μmのイオン交換膜を用いた場合では、補強膜を用いない単電池Gでは10セル中6セルにイオン交換膜の破損が見られたが、補強膜を用いた単電池Eにはイオン交換膜の破損は見られなかった。さらに10μmのイオン交換膜を用いた場合では補強膜を用いない単電池Hでは10セルすべてにイオン交換膜の破損が見られたが、補強膜

を用いた単電池Fにはイオン交換膜の破損は見られなかった。これらの結果から、補強膜を用いた場合には、イオン交換膜の膜厚が50μm以下であっても破損は起こらなかった。

【0036】図5に本発明の実施例の単電池A、EおよびFと比較例の単電池Cの無加湿作動時および加湿作動時の電流電圧曲線を示す。また、すべての単電池で加湿作動時と比較して無加湿作動の電池電圧は低下した。しかし、単電池A、EおよびFでの電圧低下が数十mVと小さいのに対し、膜厚が130μmである単電池Cでは電圧差が大きく、特に0.2A/cm²より低い電流密度で著しく低下した。

【0037】図6に本発明の実施例の単電池A、EおよびFと比較例の単電池Cの無加湿作動時および加湿作動時の電流値と内部抵抗の関係を示す。また、すべての単電池で加湿作動時と比較して無加湿作動の内部抵抗は増加したが、単電池A、EおよびFと比較して膜厚の大きい単電池Cの内部抵抗は著しく増加した。

【0038】無加湿作動の場合、生成水のみでイオン交換膜を加湿する。膜厚が小さいほどイオン交換膜を加湿するために必要な水分量は少なくよく、同じ水分量であれば膜厚が薄い膜の方がイオン交換膜の含水率は高くなり、抵抗は小さくなる。また膜厚が小さければ水の濃度勾配が大きくなり、正極で生成した水が逆拡散しやすくなりイオン交換膜が加湿されやすくなる。本実施例の単電池Aに用いたイオン交換膜の厚みは $50\mu\text{m}$ と薄い。そのため単電池Aは無加湿作動でもイオン交換膜の含水率が比較的高く内部抵抗が低くなり、加湿作動と遜色のない分極特性を示したといえる。さらに膜厚の薄いイオン交換膜を用いた単電池EおよびFではこれらの効果が大きくなり、無加湿作動が容易となり、単電池Aよりさらに高い特性を示したと考えられる。一方単電池Cはイオン交換膜の膜厚が $130\mu\text{m}$ と厚いため、生成水のみではイオン交換膜の加湿が不十分で内部抵抗が高くなり、特に生成水量の少ない低電流密度域で顕著に現れ、無加湿作動の特性が加湿作動と比較して低下したと考えられる。

【0039】図7に本発明の実施例の単電池Aと比較例の単電池B、Dの無加湿作動での電流-電圧曲線を示す。単電池A、BおよびDの開回路電圧はそれぞれ 1015mV 、 900mV 、および 1010mV であり、単電池AおよびDは単電池Bより高い値を示した。また単電池AおよびBはほぼ同じ分極特性で、単電池Dより優れた特性を示した。

【0040】単電池AおよびDが単電池Bより高い開回路電圧を示したことから、補強膜によって電極の周辺部からの反応ガスのクロスオーバーが抑制されたといえる。また単電池Dでは補強膜が電極触媒層と重なっているため電極とイオン交換膜の面積が減少する。しかし単電池Aは補強膜が電極触媒層と重ならないために電極面積が減少することなくイオン交換膜が補強されて単電池Dより優れた分極特性を示したといえる。

【0041】なお、本実施例においてイオン交換膜に米国デュボン社製のNafion膜およびジャパングアテックス(株)製のGORE-SELECTを用いたが、カチオン伝導性を示すイオン交換膜であればこれに限定されるものではない。

【0042】また補強膜にフッ素樹脂シートを用いたが、耐熱性および耐酸性を有するものであれば同様の効果が得られる。本実施例では粘着材を有するシートを用いたが、粘着材を有しないシートを熱融着等によってイオン交換膜と一体化することによっても同様の効果が得られる。さらに本実施例では厚み $50\mu\text{m}$ の補強膜を用いたが、補強膜の厚みは実施例中の厚みと限らず、イオン交換膜の厚みによって最適化する必要がある。

【0043】さらに本実施例では補強膜の周縁部とイオン交換膜の周縁部とは一致しているが、補強膜の周縁部はガス拡散層の周縁部より外側にあれば同様の効果が得られる。

【0044】

【発明の効果】以上のように本発明によれば、薄膜のイオン交換膜を用いた場合においても電極の反応面積を減少させることなく膜電極接合時、電池組立時および作動時にイオン交換膜の破損を防止でき、優れたシール性を有する固体高分子型燃料電池を実現できるものである。

【0045】また、イオン交換膜中で水素と酸素を反応させることによる水素利用率の減少することなく固体高分子型燃料電池の無加湿作動を行うことが可能となる。

【図面の簡単な説明】

【図1】本発明の一実施例における固体高分子型燃料電池の構成を示す構造図

【図2】本発明の別の実施例における固体高分子型燃料電池の構成を示す構造図

【図3】従来例における固体高分子型燃料電池の構成を示す構造図

【図4】従来例における固体高分子型燃料電池の構成を示す構造図

【図5】本発明の実施例および比較例の固体高分子型燃料電池の電流-電圧特性を示す図

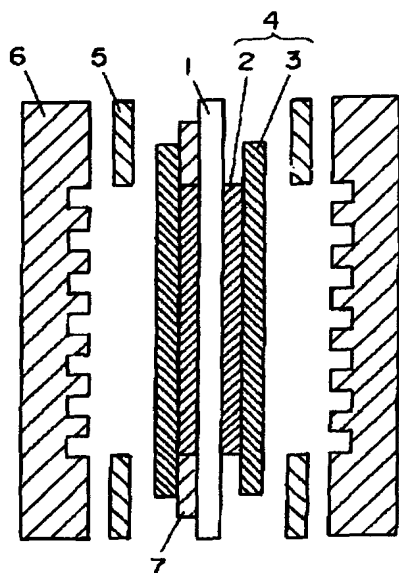
【図6】本発明の実施例および比較例の固体高分子型燃料電池の電流と内部抵抗の関係を示す図

【図7】本発明の実施例および比較例の固体高分子型燃料電池の電流-電圧特性を示す図

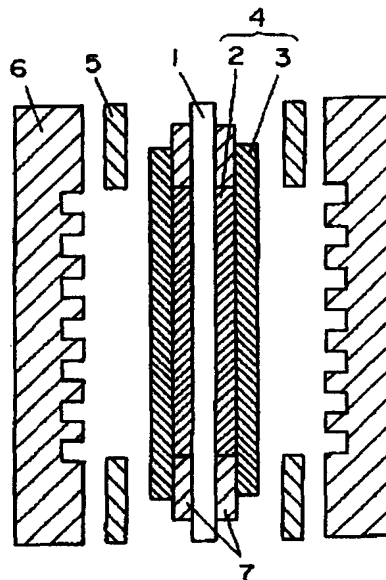
【符号の説明】

- 1 イオン交換膜
- 2 触媒層
- 3 拡散層
- 4 ガス拡散電極
- 5 ガスケット
- 6 セパレータ
- 7 補強膜

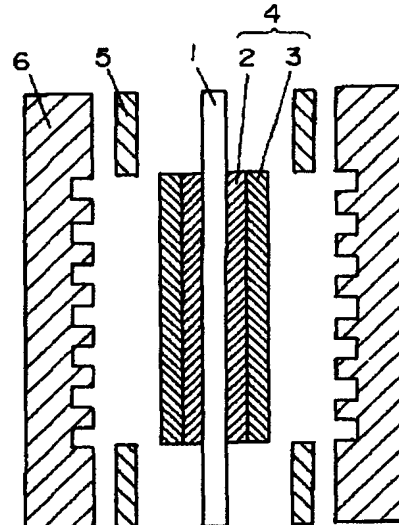
【図1】



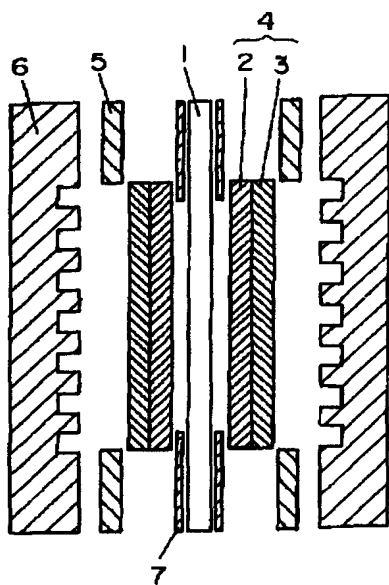
【図2】



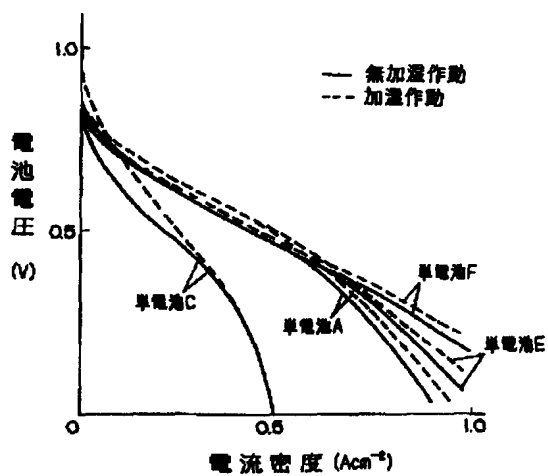
【図3】



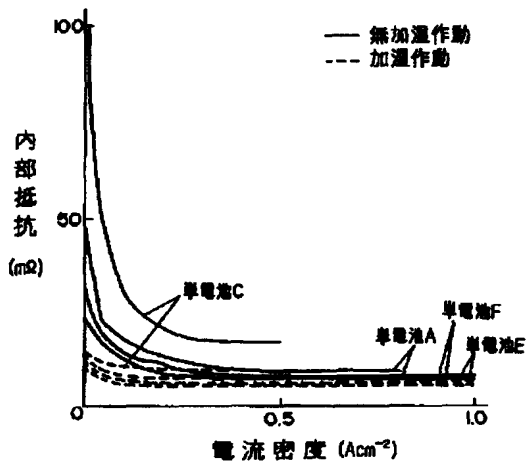
【図4】



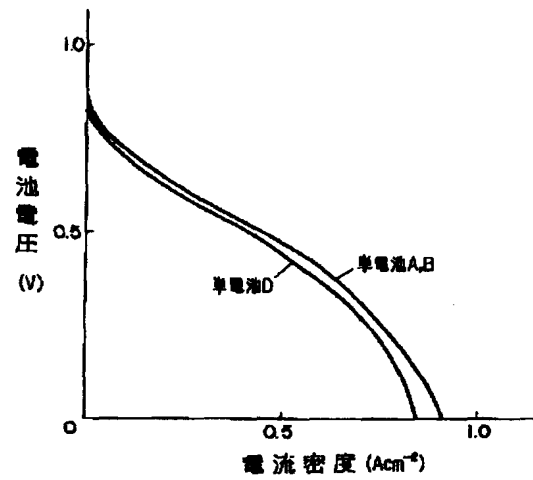
【図5】



【図6】



【図7】



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